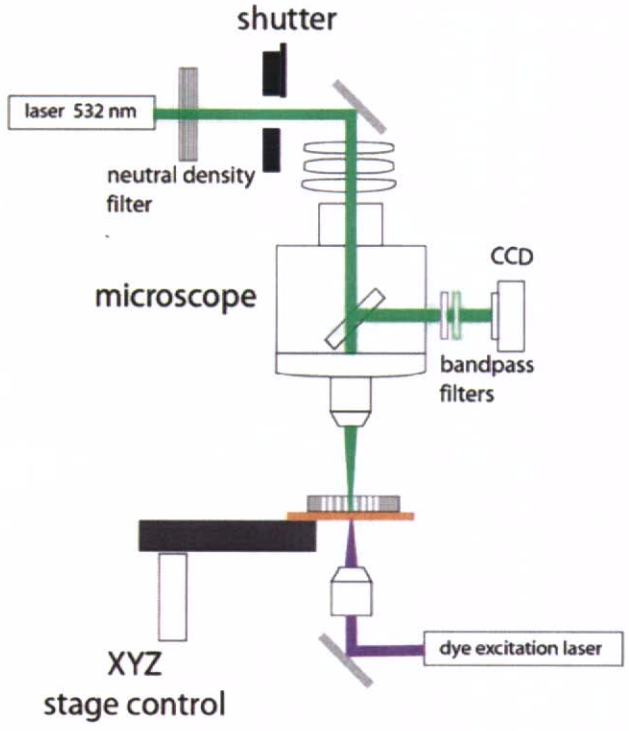

FIG. SIS-1: Experimental setup

VI. SUPPORTING INFORMATION

A. Experiment

The experimental setup is shown in Figure SIS-1. The microscope was equipped with a camera adaptor coupling a color CCD (Sony F-3103) through the eyepiece. Both white light for general illumination and a 532 nm laser diode (maximum power ~ 14 mW) were focused onto the substrate using the same 10X microscope objective. The reflected power was also measured from the other eyepiece using a Newport 1835C power meter. The 405 nm laser used for excitation in the temperature-fluorescence measurements was passed through a monochromater before being brought-in from below the sample. The beam was focused with a 10X microscope objective. The sample was mounted on a computer controlled XYZ stage.

Fluid was injected into the microchannels using a syringe and a length of Tygon tubing (Cole-Palmer ID 0.092 inches). Channels were partially filled so the air-liquid interface was near the center of the device.

B. Fabrication of Microfluidic Channels

Fluidic channels were formed using soft lithography techniques by casting of PDMS (10:1 GE-RTV 615 A:B).[15] Replica molds were created through contact lithography of a positive photoresist (SPR 220-7, Michrochem). The fabricated channels had a width of 30 μm, and measured height of 5 μm. The PDMS channels were peeled away from the molds after curing for 30 minutes at 80 °C. The PDMS chips were washed in ethanol and their surfaces were cleaned using cellophane tape (Scotch brand). Chips were placed in contact with the prepared substrates and examined for blockages, air bubbles, or other imperfections under 100X magnification. Chips with clean, unblocked channels were baked for at least 4 hours at 80 °C to form a strong reversible bond between the PDMS and the substrate.

C. Nanoparticle Arrays

The gold nanoparticle arrays were fabricated by the block copolymer lithography (BCPL) method.[4] A mixture of 25.4 mg of the diblock copolymer [polystyrene$_{81,000}$-*block*-poly(2-vinylpyridine)$_{14,200}$ (Polymer Source, Inc.) and 5 ml of toluene was stirred in a nitrogen purged and dark environment and stirred overnight, about 8 mg of $HAuCl_4 \cdot H_2O$ were added, and this solution was stirred for 90 hours. The solution was spun on to a glass microscope slide and was allowed to dry. The substrate was then placed in an oxygen plasma for 10 minutes at 75 W. The substrates were then treated in an adhesion promoting vapor (hexa-dimethyl-siloxane 100% 2 min) to render them more hydrophobic and facilitate bonding with soft-fluidic structures. An SEM image of a typical nanoparticle array is shown in Figure SIS-2, the absorbance spectrum is shown in Figure SIS-3, and the particle size distribution is shown in Figure SIS-4.

The optical transmission spectra of the arrays were taken using a dedicated microscope. The microscope has an additional objective on the condenser lens so that the light is focused on the same surface as the imaging objective. This is important because if both the objectives are not focused, we have found that interference fringes will result in the spectrum. There are also apertures for both objectives allowing good control of the stray light. Apertures of a few millimeters were used.

D. Image analysis

For the pumping measurements, edge detection techniques were implemented into Matlab to determine the position of the leading fluid edge in still frames captured every 5 seconds.[16] Linear fits were constructed using linear fitting algorithms, which are built into Matlab. In the

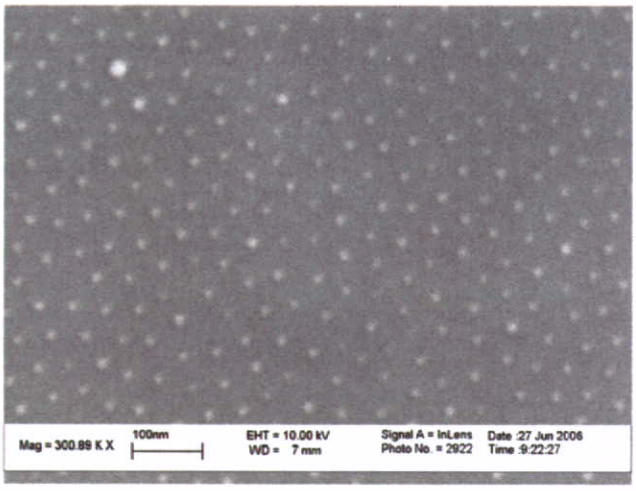

FIG. SIS-2: Scanning electron micrograph of a typical array of Au nanoparticles on SiO_2 used in this experiment. The array was produced by BCPL.

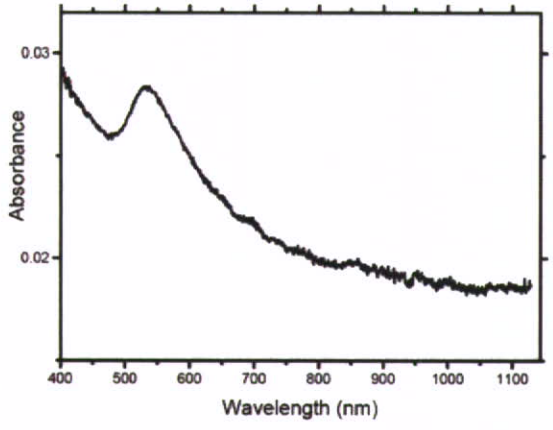

FIG. SIS-3: The absorbance spectrum of a typical nanoparticle array used in these experiments.

distillation studies, Matlab was used to compare the fluorescence intensities between images by taking the mean of identical regions of pixels in each image and using only the blue channel of the CCD image.

Images of the channel were captured every 5 s during pumping. The position of the free-surface with time was determined from the images using Matlab's edge detection techniques and built in linear fitting algorithms. In the distillation, fluorescence intensity was compared between images by taking the mean of identical regions of pixels in each image, using only the blue channel of the image.

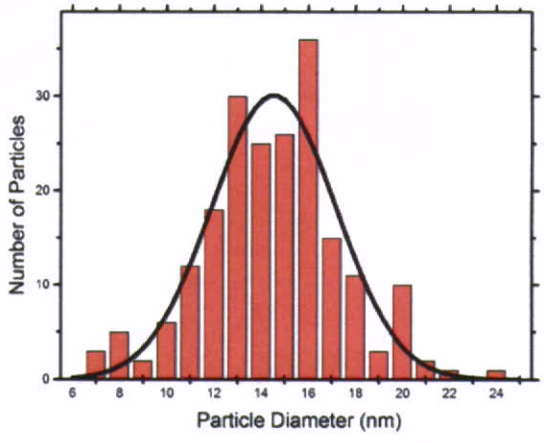

FIG. SIS-4: The distribution of nanoparticle diameters from Figure SIS-2. The solid line is a Gaussian fit. The mean is 14.5 nm and the standard deviation is 2.6 nm

E. Distillation measurements

The distillation studies were performed using a mixture of 0.1 M Coumarin 4 dye (peak emission 420 nm)(Exciton) in pure ethanol, with a temperature dependent buffer of HCL and tris (hydroxymethyl)aminomethane (Tris buffer)[17]. The pH of this mixture was adjusted via titration with added buffer solution to the point of maximum sensitivity with temperature. The dye was excited using a 405 nm solid state laser (5 mW) focused to the approximate field of view of the camera. Fluorescence images were recorded through a band pass filter centered around 420 nm (Semrock) with an exposure of 15 s. The maximum temperature sensitivity was calibrated using a thermocouple and a Peltier cooler, and was determined to be around 2 °C. Fluorescence quenching was linearly proportional to temperature over a range of 25-55 °C. We did not observe significant photo-bleaching of the solution.

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[16] Ziou, D.; Tabbone, S. *International Journal of Pattern Recognition and Image Analysis* **1998**, *8*, 537–559.
[17] Ross, D.; Gaitan, M.; Locascio, L. *Anal. Chem* **2001**, *73*, 4117-4123.